

Synthesis and Characterization of Nickel (II) Complexes Derived from Pyrano [2, 3-d] Pyrimidines

Hoda Pasdar*, Sahar Shaygan, Naser Foroughifar, Mehran Davallo, Fereshteh Motiee

Faculty of Chemistry, North Tehran Branch, Islamic Azad University, Tehran, Iran

Abstract: In this paper, the syntheses and characterization of bidentate pyrano [2, 3-d] pyrimidine ligands and their Ni (II) complexes are reported. Magnetic nanoparticles N-propyl-benzoguanamine-SO₃H were used as a catalyst for the synthesis of the ligands. The molecular structures of Nickel complexes based on these ligands are described as square planner geometry. The complexes are characterized by FTIR, UV-Vis, molar conductance and mass spectroscopy. The low molar conductance values indicated that the complexes are nonelectrolytes.

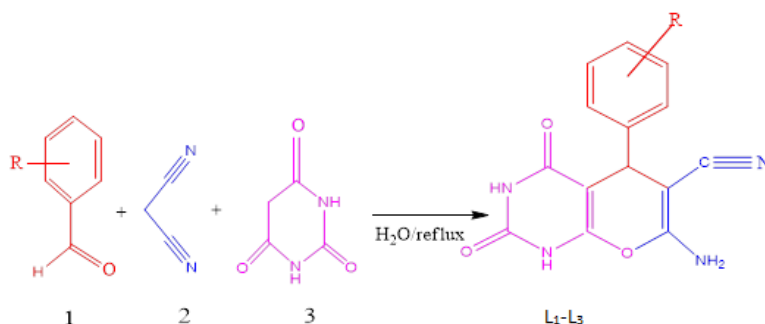
Keywords: Bidentate ligand, Pyrano [2, 3-d] pyrimidine, Ni(II) complexes, Square planner geometry.

1. Introduction

Recently, heterocyclic compounds have received special attention according to their many notable biological activities [1-4]. Among the others, pyrimidine derivatives are highly regarded because they have shown many biological properties especially as anti-inflammatory, antimicrobial, anti-hypertensive, anti-HSV-1 and antibacterial activities [5-7]. Many attempts have been made to design convenient procedures to syntheses heterocyclic compounds. The most important and popular method is Multi-component reactions (MCRs). MCRs are reactions in which three or more substances react in one step in a single flask to form a new product [8]. The first modern contribution to the development of multicomponent chemistry was made in 1850 by Strecker [9]. The crucial step in the well-known strecker synthesis is the formation of α -amino nitriles from aldehyde, an amine and alkaline metal cyanide in one-pot. This method allows molecular complexity and diversity to be created by the facile formation of several new covalent bonds [10]. The advantage of this method is that the procedure is simple, atom economy, environmental concerns and profit from avoiding unnecessary separation and purification procedures [11-13].

The solvent and inexpensive catalyst for MCRs plays an important role in syntheses of products. Pyrano [2, 3-d] pyrimidine derivatives have been reported using different catalyst such as trisodium citrate, K₂CO₃, DABCO and dibutylamine [14-17]. Fe₃O₄ based magnetic nanoparticles (MNPs) as a powerful strategy in organic synthesis has shown excellent features due to such as easy preparation and functionalization, considerable durability and reusability, high surface area, nontoxic and facile removing with aid of external magnet [18-20].

During the last decade the N-heterocyclic compounds and their derivatives have been used continuously as ligand in coordination chemistry [21]. This group of ligands include the family of pyrano pyrimidines which are known to have a great value in medicinal chemistry due to a variety of biological activates such as antibacterial, anti-tumor, anti-viral which have been related to their chelating ability with metal ions [22-24]. In this work we prepare Nickel (II) complexes of pyrano pyrimidines derived from condensation of barbituric acid, malononitlre and aldehyde aromatics with MNPs-N-propyl-benzoguanamine-SO₃Hcatalyst. The method of synthesis for ligands is illustrated in Scheme 1.



Scheme 1: Syntheses of pyrano [2, 3-d] pyrimidine derivatives

2. Experimental

Material and methods

Chemicals were purchased from Merck Company. The FTIR spectra (KBr), in the range of 4000-450 cm^{-1} , were recorded on a standard stambd 3577 Bruker FTIR spectrometer. The UV-Vis spectra of the compounds were recorded on a Bio-TEK, kon TRON 922 spectrophotometer. The progress of the reaction was monitored by thin-layer chromatography TLC (thin-layer chromatography) using $\text{CH}_2\text{Cl}_2/\text{EtOAc}$ (3:1) as an eluent.

General procedure for the synthesis of pyrano [2, 3-d] pyrimidine derivatives (L_1 - L_3)

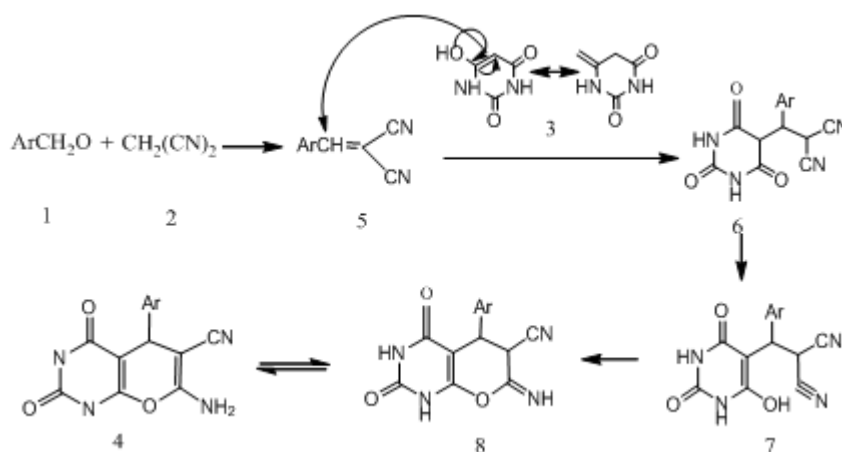
MNPs-N-propyl-benzoguanamine- SO_3H catalyst was prepared by chemical co-precipitation according to the previous literature [25]. Substituted aromatic aldehyde (1mmol), malononitril(1mmol), barbituric acid (1mmol) and MNPs-N-propyl-benzoguanamine- SO_3H catalyst (6mg) were added to a 10 mL aqueous media flask and refluxed for 5-6 h. The progresses of the reactions were monitored by TLC. The solid product was filtered and recrystallized with hot ethanol to obtain pure pyrano [2, 3-d] pyrimidine derivatives with excellent yields.

Syntheses of the Ni (II) complexes

A solution of (L_1 - L_3)(2mmol) in 15 mL of DMSO was added drop-wise to a solution of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in 5 mL DMSO for preparation of complexes. The reaction mixture was refluxed for about 5 h. The solutions were then evaporated under vacuum. The completion of reaction was monitored with TLC.

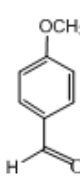
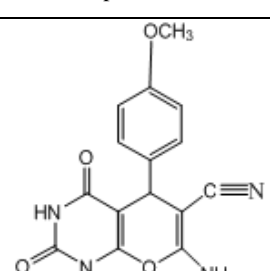
3. Results and Discussion

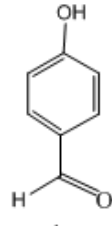
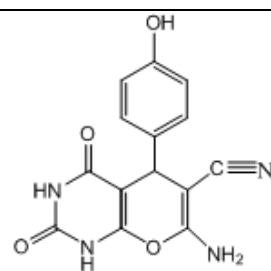
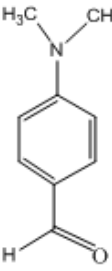
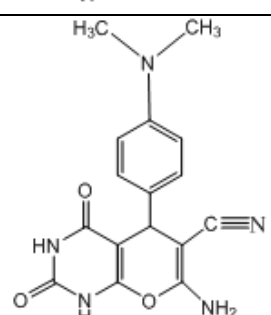
A possible mechanism is shown in Scheme 2. The reaction was carried out via condensation of an aqueous solution of aldehyde, malononitrile and barbituric acid in one step. The complexes were synthesized by the reaction between ligands and metal ion2:1 molar ratio. The ligands and metal complexes were quite stable at room temperature and soluble in DMSO and DMF. The molar conductance of 10^{-3} M solutions of the complexes in DMSO at room temperature have been observed in the range 12-16 $\Omega^{-1}\text{mol}^{-1}\text{cm}^2$ suggesting that they are nonelectrolytes.



Scheme 2: A possible mechanism for preparation of (L_1 - L_3)

Table 1: Synthesis of pyrano [2, 3-d] pyrimidine derivatives (L_1 - L_3)

aldehyde	product	yield %	M.P. (°C)
 a		92	290

 b		95	160
 c		90	295

FTIR spectra

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The FTIR bands of ligands and metal complexes are listed in Table 2. The FTIR spectrum of the complexes shows that the ligands behave as bidentate and coordinate via cyano ($C\equiv N$) and Amin groups. In the ligands $C\equiv N$ group shows at 2100 cm^{-1} but in metal complexes no band was observed in this wavelength. The presence of new band in the metal complexes in the region 1600 cm^{-1} can be related to $C=N$ group.

Table 2: FTIR spectral data of the ligands and metal complexes

Compounds	$\nu(N-H)$	$\nu(C\equiv N)$	$\nu(C=N)$
L_1	3372	2186	-
L_2	3257	2195	-
L_3	3330	2191	-
NiL_1	3420	-	1660
NiL_2	3441	-	5166
NiL_3	3414	-	1654

Electronic absorption spectra

The UV-Vis spectra of pyrano-pyrimidine ligands and their metal complexes were recorded in DMSO as solvent. The ligands show bands in range 290-320 nm which is assigned to $\pi \rightarrow \pi^*$ transition. In the UV-visible spectra of complexes slight shifts to the lower wavelength are observed in the position of this band as compared to the ligands. The NiL_1 , NiL_2 and NiL_3 complexes showed bands at 420, 450 and 470 nm, respectively. These bands correspond to $A_{2g} \rightarrow E_g$ transitions; and confirmed square planar geometry for all the complexes. The band positions are presented in Table 3.

Table 3: UV-Visible data of ligands and complexes

Compounds	Assignment	Band position (nm)
L_1	$\pi \rightarrow \pi^*$	290
L_2	$\pi \rightarrow \pi^*$	300
L_3	$\pi \rightarrow \pi^*$	320
NiL_1	$\pi \rightarrow \pi^*$, ${}^3A_{2g} \rightarrow {}^3E_g$	250, 420
NiL_2	$\pi \rightarrow \pi^*$, ${}^3A_{2g} \rightarrow {}^3E_g$	240, 300, 450
NiL_3	$\pi \rightarrow \pi^*$, ${}^3A_{2g} \rightarrow {}^3E_g$	250, 470

Mass spectral studies

The mass spectra of the complexes are in good agreement with the proposed structures. The molecular ion peaks for the NiL_1 , NiL_2 and NiL_3 complexes were observed at $m/z = 680$, 653 and 706 , respectively. The other peaks in the mass spectrum were attributed to the fragmentation of the complex obtained from the rupture of different bonds inside the molecule. The proposed structure of metal complexes is shown in Figure 1.

Figure 1: Proposed structure for metal complexes

4. Conclusion

The corresponding pyrano-pyrimidine ligands (L_1 - L_3) was prepared from reaction aromatic aldehyde, malononitril, barbituric acid in the presence of MNPs-N-propyl-benzoguanamine- SO_3H as catalyst in good yield. In the next step, The nickel (II) complexes were prepared by reaction of ligands and metal salt in molar ratio 2:1(L:M). All the synthesized compounds were characterized with FTIR, UV-Visible and mass spectroscopy. For all the complexes square planar geometry were proposed.

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